

Process for the desulphurization of a mixture of hydrocarbons

The present invention relates to a process for the desulphurization of a mixture of hydrocarbons, such as petroleum fractions, for example engine fuels, comprising sulphur compounds. The process comprises a stage of oxidation, in order to oxidize the sulphur compounds, which is followed by a stage of removal
5 of the oxidized compounds by adsorption on an adsorbent solid.

For environmental reasons, specifications with regard to the sulphur content of engine fuels are becoming increasingly strict and methods which make it possible to reduce this content have therefore been developed. The conventional process for removing sulphur from petroils is based on the
10 hydrodesulphurization reaction represented by



where RSR' represents an aliphatic, alicyclic or aromatic sulphur compound. There are a number of disadvantages to this known process. For example, observing the new sulphur specifications requires more stringent
15 hydrodesulphurization conditions (excess of hydrogen, higher temperature, higher pressure, and the like) and necessarily results in an increase in the cost of the engine fuels. In addition, some sulphur compounds found in petroleum fractions, such as substituted benzothiophenes and dibenzothiophenes, such as, for example, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene, are
20 highly resistant to 'hydrodesulphurization. The sulphur which is present therein is therefore difficult to remove by this route. On the other hand, these compounds are relatively easy to oxidize.

Consequently, processes comprising a stage of oxidation of the sulphur compounds, followed by a stage of removal of these oxidized compounds, have
25 been developed. In these, the oxidized compounds can be removed by various means, for example by physical treatment, such as extraction by a solvent which is immiscible with the engine fuel, or by adsorption on a solid or also by distillation or by precipitation under cold conditions. The removal can also be a chemical treatment of the pyrolysis or alkaline hydrolysis type.

30 In comparison with an extraction using a solvent, adsorption on a solid has a number of advantages:

- no significant losses of the extracting agent

- industrial plants which is generally simpler.

Thus, in Patent GB 2 262 942, two adsorbent solids (silica and alumina), used alone or one after the other, in two separate layers, were tested on oxidized fuels. The lowest residual sulphur content obtained with these adsorbent solids is
5 50 ppm.

The Applicant Company has carried out desulphurization tests on mixtures of oxidized hydrocarbons in attempting to bring the residual S to below 50 ppm and has found that the selectivity is not optimum with this type of adsorbent solid, that is to say that there is a not insignificant loss of hydrocarbons, (by
10 nonselective adsorption). It is the same with crystalline silicas/aluminas (clays or zeolites). On the other hand, the Applicant Company has found that, surprisingly, the selectivity obtained is markedly better when a solid comprising at least 60% by weight of amorphous silica/alumina is employed as adsorbent solid.

The invention consequently relates to a process for the desulphurization of
15 a mixture of hydrocarbons comprising sulphur compounds, comprising a stage of oxidation by means of an oxidizing agent, in order to oxidize the sulphur compounds, followed by a stage of removal of the oxidized sulphur compounds by adsorption on an adsorbent solid, in which the adsorbent solid comprises at least 60% by weight of amorphous silica/alumina.

20 The term "mixture of hydrocarbons" is understood to denote any product predominantly comprising hydrocarbons, such as paraffins, olefins, naphthenic compounds and aromatic compounds. It can be crude oil or a petroleum derivative obtained by any known refining treatment. The mixture of hydrocarbons can be chosen from petroleum fractions involved in the
25 composition of any type of engine fuel and fuel. Mention may be made, among these, of kerosene, motor vehicle engine fuels, such as petrol or diesel, and domestic fuels, such as, for example, heating oil.

Particularly advantageous results are obtained when the mixture of hydrocarbons which is subjected to the oxidation stage comprising hydrocarbons
30 with 10 or more carbon atoms (in particular from 10 to 50 carbon atoms and generally from 10 to 40 carbon atoms) in an amount of greater than 50% by weight, in particular of greater than or equal to 60% by weight.

The process according to the invention proves to be particularly effective when the mixture of hydrocarbons comprises aromatic hydrocarbons in an
35 amount of less than or equal to 80% by weight, in particular of less than or equal to 60% by weight, values of less than or equal to 50% by weight giving

particularly good results. The term "aromatic hydrocarbons" is understood to denote any compound quantitatively determined by the method described in Standard IP 391 (1995). Without wishing to be committed to a theory, the Applicant Company believes that an excessively high content of aromatics is 5 capable of reducing the selectivity of the process in view of the polar nature of these molecules and thus of their affinity with regard to the adsorbent solid.

In the process according to the invention, the oxidation stage can be preceded by one or more other stages, such as the conventional stages of a refining process. Particularly outstanding results are obtained when the oxidation 10 stage is preceded by one or more hydrodesulphurization (HDS) stages. Thus, preferably, the sulphur content of the mixture of hydrocarbons treated by the process according to the present invention is advantageously less than or equal to 200 ppm, indeed even less than or equal to 100 ppm, and preferably even less than or equal to 50 ppm. At these low sulphur contents, the oxidized sulphur 15 compounds are in fact particularly difficult to selectively remove from the oxidized mixture of hydrocarbons.

The term "sulphur compounds" is understood to denote any pure substance and any compound present in the mixture of hydrocarbons which comprises sulphur. They are in particular benzothiophene, dibenzothiophene, 20 benzonaphthothiophene and their mono- or polysubstituted derivatives, more specifically 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene.

The term "desulphurization" is understood to denote any treatment which makes it possible to reduce the sulphur content of the mixture of hydrocarbons.

The sulphur compounds can be oxidized, for example, to corresponding 25 sulphoxides, sulphones and sulphonic acids.

The oxidizing agent used in the process according to the invention can be chosen from gaseous oxygen, hydrogen peroxide, ozone, nitrogen oxides, nitric acid, organic (carboxylic, sulphonic and phosphonic) peracids, inorganic 30 peracids (Caro's acid, perboric acid), chlorine, inorganic and organic hypochlorites, hydroperoxides and persalts (perborate, percarbonate). An oxidizing agent comprising hydrogen peroxide is preferred.

According to a first alternative form, hydrogen peroxide can be employed in the presence of a carboxylic acid (such as acetic acid) and an acid catalyst, so as to form, in situ or in a separate reactor, the corresponding peracid (such as 35 peracetic acid), which is the substance which oxidizes the sulphur compounds. This first alternative form is used in the copending French patent application of

the Applicant Company, filed on 26.02.2001 under the number 01.02688, the content of which is incorporated by reference in the present patent application.

According to a second alternative form, hydrogen peroxide can be employed in the presence of a solid catalyst, the active sites of which are 5 activated by hydrogen peroxide so as to be able to oxidize the sulphur compounds. This second alternative form is used in the copending French patent application of the Applicant Company, filed on 09.05.2001 under the number 01.06151, the content of which is incorporated by reference in the present patent application.

10 Finally, according to a third alternative form, hydrogen peroxide can be employed in the presence of an acid catalyst, at least a portion of which forms a separate phase in the reaction medium and which comprises acid groups capable of reacting with hydrogen peroxide to form an agent which oxidizes sulphur compounds. This third alternative form is used in the copending French patent 15 application of the Applicant Company, filed on 14.02.02 under the number 02.01881, the content of which is incorporated by reference in the present patent application.

In the process according to the invention, the oxidation and adsorption 20 stages can be separated by one or more other stages, such as filtration, aqueous washing, destruction of the residues from the oxidizing agent, extraction by means of a solvent, stripping or distillation.

The adsorption stage in the process according to the present invention consists in bringing the mixture of hydrocarbons comprising oxidized sulphur 25 compounds into contact with an adsorbent solid, preferably with a contact time and a mixture to be treated/adsorbent solid ratio by weight suited to the desired degree of desulphurization. This contacting operation can be carried out in any type of appropriate equipment. It can be carried out batchwise in a reactor in which the adsorbent solid is suspended. However, the contacting operation is 30 preferably carried out continuously in an adsorption column filled with a fixed bed of adsorbent solid through which the mixture of hydrocarbons is eluted. In this case, the amount of adsorbent solid present in the column, the elution rate, the adsorption temperature and the adsorption pressure are to be optimized according to the desired degree of desulphurization. Generally, care will be taken 35 to obtain an elution rate of between 20 and 40 cm/min, excessively high rates resulting in an excessive pressure drop and excessively low rates resulting in preferential elution pathways. As regard the temperature, the latter is preferably

not very high. Temperatures of approximately 20°C are generally highly suitable.

The process according to the present invention can be a continuous or batchwise process. It is preferably a continuous process, that is to say that both 5 the oxidation and adsorption stages are carried out continuously and use, in order to do this, at least one oxidation reactor and at least one adsorption column.

Given that the oxidized sulphur compounds present in the mixture of hydrocarbons are gradually adsorbed on the adsorbent solid and that the active sites of the latter are gradually saturated, it is generally advisable to regularly 10 regenerate the adsorbent solid by any appropriate method (calcination under air, displacement by means of polar solvent(s) and the like). Consequently, in the case of a continuous process, it is often necessary to plan for several adsorption columns in order to provide operation/regeneration cycles.

The term "silica/alumina" is understood to denote compounds comprising 15 silica and alumina and in which at least a portion of the silica and at least a portion of the alumina have reacted to form Si-O-Al bonds. Physical mixtures of pure silica and of pure alumina do not correspond to this definition. The silicas/aluminas used in the process according to the present invention can be obtained by any known process, for example by one of those described by 20 K. Fogler ("Dispersed Metal Catalysts", Catalysis, Science & Technology, edited by J.R. Anderson and M. Boudart, Springer Verlag, 1984, V 6, p.232).

Generally, the silica/alumina ratio by weight in the silica/alumina used in the process according to the present invention is between 99:1 and 1:99. However, preferably, the alumina content is less than or equal to 50% by weight 25 (with respect to the total weight of the dry solid, that is to say after removal of the physisorbed water), indeed even less than or equal to 30% by weight and more particularly less than or equal to 20% by weight. However, this content is advantageously greater than or equal to 2% by weight and preferably greater than or equal to 3% by weight. The Applicant Company has found that a low alumina 30 content gives good results both in terms of selectivity and of adsorption capacity. Without wishing to be committed to a theory, the Applicant Company believes that silicas/aluminas with a low alumina content exhibit strong acid sites which interact with the oxidized sulphur compounds, which exhibit a slightly basic nature.

35 The term "amorphous" is understood to characterize a structure which does not exhibit an X-ray diffraction line (in contrast to crystalline structures, which

exhibit at least one such line). In the process according to the present invention, the adsorbent solid used:

- is either essentially composed of an amorphous structure as defined above and thus is devoid of any solid of crystalline structure,
- 5 – or comprises a solid of crystalline structure but in amounts of less than or equal to 40% and in particular of less than or equal to 20% by weight (with respect to the total weight of the dry adsorbent solid). An example of solid of crystalline structure is crystalline silicas/aluminas (clays, zeolites). Zeolites X and Y (of faujasite type) give good results. More particularly, cracking catalysts composed of a matrix of amorphous silica/alumina in which a zeolite X or Y, preferably exchanged by a rare earth metal, is dispersed give good results. The choice of such an adsorbent solid makes it possible to optionally couple its regeneration with that of a cracking catalyst, for example by calcination under air actually within a catalytic cracking unit.
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- 15 The adsorbent solid used in the process according to the present invention preferably has a content of silica/alumina (amorphous and/or crystalline) of greater than or equal to 95% by total weight of the dry solid and preferably of greater than or equal to 98% by total weight of the dry solid. The adsorbent solid can, in some cases, comprise oxides of other elements, such as alkali metals, alkaline earth metals, rare earth metals, Ti, Fe or Zr. These oxides are generally present in a content of less than or equal to 5% by weight, indeed even of less than or equal to 2% by weight. Without wishing to be committed to a theory, the Applicant Company believes that the presence of a small amount of rare earth metal in the adsorbent solid makes it possible to reduce the temperature for regeneration by calcination and thus to limit sintering phenomena.
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The adsorbent solids used in the process according to the present invention make it possible to achieve a thorough desulphurization and ratios by weight of the mixture of hydrocarbons to be treated to the amount of adsorbent solid required which are very high. In addition, as mentioned above, they make it possible to increase the selectivity of the adsorption, that is to say to limit the nonselective adsorption of sulphur-free hydrocarbons. By the choice of an appropriate specific surface and of a specific porosity (see below), it is possible to optimize the results obtained both in terms of capacity and of selectivity.

30 Thus, in the process according to the present invention, the adsorbent solid preferably exhibits a specific surface (determined by the BET equation derived from the analysis of the nitrogen adsorption isotherms: Ref. Adsorption by

Powders and Porous Solids, Principles, Methodology and Applications, F. Rouquerol, J. Rouquerol and K. Sing, 1997, Academic Press, pp. 166-174) of greater than or equal to 400 m²/g, indeed even of greater than or equal to 500 m²/g. However, this specific surface is generally less than or equal to 1000 m²/g, 5 indeed even less than or equal to 800 m²/g and even less than or equal to 700 m²/g.

In addition, in the process according to the present invention, the adsorbent solid preferably comprises mesopores (that is to say, pores with a mean diameter of between 2 and 50 nm). The presence of mesopores can be established on the 10 basis of the shape of the gas physisorption isotherm according to the IUPAC classification (Ref. Adsorption by Powders and Porous Solids, Principles, Methodology and Applications, F. Rouquerol, J. Rouquerol and K. Sing, 1997, Academic Press, pp. 18-19). Mesopores are present when this curve is of IV type. However, it should be noted that the presence of mesopores does not 15 preclude the simultaneous presence of micropores (pores with a size of less than 2 nm) in the solid.

The adsorbent solid used in the process according to the invention generally exhibits a pore volume (measured by the nitrogen adsorption/desorption technique; Ref. Adsorption by Powders and Porous Solids, 20 Principles, Methodology and Applications, F. Rouquerol, J. Rouquerol and K. Sing, 1997, Academic Press, pp. 166-174) of greater than or equal to 0.1 cm³/g, in particular of greater than or equal to 0.2 cm³/g and preferably of greater than or equal to 0.5 cm³/g. The pore volume is usually less than or equal to 5 cm³/g, more especially less than or equal to 3 cm³/g, the values of less than or equal to 25 1.5 cm³/g being the commonest.

In the process according to the invention, the adsorbent solid is generally employed in the form of particles which can be obtained by any known process. The most diverse particle shapes are conceived, such as, in particular, powders, beads, pellets, extrudates or honeycomb structures. The adsorbent solid can be 30 employed in suspension or in the form of a fixed bed. The mean size of these particles depends on the type of use. For a process where the adsorbent solid is in suspension, the mean size of the particles is generally greater than or equal to 5 µm, more particularly greater than or equal to 10 µm and very particularly greater than or equal to 50 µm. The mean size of the particles is usually less than 35 or equal to 500 µm, more particularly less than or equal to 250 µm and very particularly less than or equal to 150 µm. Mean sizes of greater than or equal to

100 µm and less than or equal to 125 µm are very particularly suitable. For a process where the adsorbent solid is used as a fixed bed, the mean size of the particles is generally greater than or equal to 0.5 mm, more particularly greater than or equal to 1 mm and very particularly greater than or equal to 2 mm. The
5 mean size of the particles is commonly less than or equal to 10 mm, more particularly less than or equal to 5 mm and very particularly less than or equal to 4 mm.

An additional advantage of the process according to the present invention
is that it furthermore makes possible the removal of the nitrogen compounds
10 present in the mixtures of hydrocarbons.

Finally, it should be noted that, in the process according to the invention,
the adsorbent solid is preferably dried before it is used in order to remove the
physisorbed water. This can be carried out by any appropriate method, for
example by drying under vacuum at 100°C for 12 h.

15 Examples:

- The examples below illustrate the present invention in a nonlimiting way.
In these:
1. A sample of hydrotreated Straight Run Gas Oil (SRGO), which is the product
of an HDS treatment carried out on the "middle distillates" fraction resulting
20 from a straight run distillation of crude oil at atmospheric pressure, was used.
The characteristics of this mixture of hydrocarbons are shown in Table 1.

Table 1: Characteristics of the mixture of hydrocarbons

Characteristic (unit)	Value
[Aromatics] by HPLC (IP 391/95) (weight %)	
Monoaromatics	23.4
Diaromatics	3.5
Triaromatics	0.3
TOTAL	27.2
[S] by X-ray fluorescence X (XRF) (wppm)	39
[S] by pyrofluorescence (wppm) (combustions/UV fluorescence)	34
[S] by Wickbold (wppm)	31
[N] by chemoluminescence (wppm)	12
[Basic N] by titration (wppm)	<0.1
Density at 15°C	0.8375
ASTM D86 distillation (°C)	
IBP	203
5 vol%	235
10 vol%	248
20 vol%	261
30 vol%	270
50 vol%	285
60 vol%	292
70 vol%	301
80 vol%	312
90 vol%	317
95 vol%	339
FBP	348
Viscosity at 40°C	3.42

2. The following adsorbent solids were used:

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|----|------------------------|--|
| 5 | Merck silica gel 60 | Aldrich, 70-230 mesh, mean diameter of the pores 60Å, specific surface 529 m ² /g, pore volume 0.72 cm ³ /g; batch 33266-050 |
| | Merck silica gel 10180 | Aldrich, 70-230 mesh, mean diameter of the pores 40Å, specific surface 750 m ² /g; batch 32665-010 |
| 10 | Dynocel 600 alumina | Porocel, 90-98% Al ₂ O ₃ , 420-590 µm, 376 m ² /g, batch 1PA-0073 |

	Silica/alumina 1	Akzo-Ketjen C25, 13.1 weight% Al ₂ O ₃ , 75 µm, 495 m ² /g, 0.71 cm ³ /g
	Silica/alumina 2	Grace, 3.8 weight% Al ₂ O ₃ , 45-125 µm, 417 m ² /g, 0.92 cm ³ /g
5	Silica/alumina 3	Nikki N631L, 13 weight% Al ₂ O ₃ , 45-125 µm, 423 m ² /g, 0.49 cm ³ /g
	Silica/alumina 4	Grace, 13 weight% Al ₂ O ₃ , 40-80 µm, 541 m ² /g, 0.77 cm ³ /g
	Cracking catalyst	Akzo, Zeolite Fluid Cracking Catalyst - M.Z.-1, 13.0 weight% Al ₂ O ₃ , < 10 weight% of zeolite Y, 40-80 µm, 627 m ² /g, 0.74 cm ³ /g
10	Zeolite Y	Zeolyst International, 657 m ² /g, [Al ₂ O ₃] = 2.1 weight%, ZD99062, batch 001-91, 45-125 µm
	Attapulgite clay	Engelhard, Attapulgite 30/60 AA-LVM, 250-500 µm, 125 m ² /g
15	Montmorillonite clay	Girdler, montmorillonite K10, 63-125 µm, 220-270 m ² /g
	Activated bauxite	Porocel, Purocel RI, 77.7% Al ₂ O ₃ /10.8% SiO ₂ /6.5% Fe ₂ O ₃ /5.0% TiO ₂ , 420-840 µm, 202 m ² /g, batch 1PB-0005
20		3. With the exception of the test which is the subject of Example C11 (not in accordance with the invention), all the tests were carried out on a mixture of hydrocarbons which is oxidized beforehand according to the following procedure:

25 Acetic acid AcOH (90.750 g), sulphuric acid (2.2987 g) and SRGO (964.170 g) were successively introduced into a jacketed Pyrex reactor provided with a paddle stirrer made of glass and of Teflon® fluoropolymer, with a point for introducing nitrogen within the solution (sparging), with a reflux condenser maintained at -25°C, with a system for adding a 39 weight % hydrogen peroxide solution and with a point for withdrawing samples. 115.125 ml of the H₂O₂ solution were subsequently introduced at a rate of 50 ml/min using a metering pump; this operation constituted the time zero of the reaction. The reaction medium was kept stirred (575 revolutions/minute) at 25°C for 1 h and was then brought to 50°C for 2 h. The colour of the organic phase changed from yellow to orange. The phases were then separated and the organic phase was also washed with 3 times 100 ml of water. Analysis of the organic phase by gas

chromatography with specific detection of sulphur (GC-AED) indicated complete conversion of the sulphur compounds present in the starting petroleum feedstock. The S content of the oxidized sample was 35 wppm by X-ray fluorescence.

- 5 4. Tests with fractionation (exploratory tests, the purpose of which is to determine the capacity of the adsorbent solid) were carried out according to the following procedure:

10 100 ml of SRGO oxidized by the $\text{H}_2\text{O}_2/\text{AcOH}/\text{H}_2\text{SO}_4$ system were passed onto a column of adsorbent solid (1 g placed in a 50 ml graduated pipette). The solid was dried beforehand in an oven under vacuum at 100°C for 16 h. The SRGO flowrate was adjusted to 1-2 ml/min. Five fractions of 20 ml were collected and weighed. The S content of these fractions was measured by X-ray fluorescence and the results obtained were considered in their entirety.

- 15 5. Tests without fractionation (where the optimum amount of SRGO for the amount of adsorbent solid available is used, using the result of exploratory tests) were carried out according to the following procedure:

20 SRGO (in an amount which depends on the nature of the mixture of hydrocarbons and on that of the adsorbent solid) oxidized by the $\text{H}_2\text{O}_2/\text{AcOH}/\text{H}_2\text{SO}_4$ system (except in the case of Example C11) was passed onto a column of adsorbent solid (1 g placed in a 25 or 50 ml graduated pipette) dried beforehand in an oven under vacuum at 100°C for 16 h. The flow rate was adjusted to 1-2 ml/min. A single fraction per test was collected and weighed, and its S content was determined by X-ray fluorescence (XRF) and/or by Wickbold combustion and quantitative determination of the sulphates by capillary electrophoresis.

- 25 6. The following were calculated:

- the capacity of the adsorbent solid, expressed in mg of sulphur adsorbed per g of adsorbent solid;
- the percentage of S removed (% S removed), defined as being the percentage of moles of S which have been removed from the mixture of hydrocarbons by adsorption; this value is rather different from the variation in the S content of the mixture of hydrocarbons ([S] difference), which value is influenced by the adsorption of hydrocarbons from the oil on the adsorbent solid;
- the yield of mixture of hydrocarbons after adsorption, defined as the ratio of the weight of the mixture of hydrocarbons after adsorption to the weight of the mixture of hydrocarbons initially employed;

- the efficiency factor K, defined by Zannikos [Zannikos F., Lois E. and Stournas S., Fuel Processing Technology, 1995, V 42, P 35-45] as the ratio of the % S removed to the fraction of the mixture of hydrocarbons which was lost by nonselective adsorption; this quantity characterizes the selectivity of the adsorption process;
- the optimum weight of hydrocarbons w (in g) per 1 g of adsorbent solid, if complete desulphurization is desired.

The results of the tests and calculations carried out appear in Tables 2 and 3 below:

TABLE 2

Adsorbent	Example	%Al2O3 (weight %)	Specific surface (m²/g)	Capacity (mg S/g)	%S removed (%)	% difference [S] (%)	Diesel yield (%)	K = %S removed / (100 - diesel yield)	Optimum diesel w per 1 g of adsorbent (g)
<i>With regard to oxidized SRGO</i>									
Merck silica 60	C1	529	1.9	57%	57%	98.8%	48	50.0	
Merck silica 10180	C2	750	1.8	56%	56%	98.3%	34	47.2	
Dynoet 600 alumina	C3	376	0.4	10%	12%	99.1%	11	9.6	
Silica/alumina 1	4	495	3.0	94%	94%	98.8%	77	75.8	
Silica/alumina 2	5	3.8	417	2.8	84%	84%	98.2%	46	71.5
Silica/alumina 3	7	13	423	2.1	70%	70%	98.7%	54	53.9
Silica/alumina 4	6	13	540	2.8	95%	95%	98.8%	82	70.8
Cracking catalyst	7	13	627	2.8	96%	96%	98.2%	52	70.7
Zelite Y	C8	21	657	1.2	44%	43%	98.5%	29	32.0
Attapulgite	C9	125	0.4	12%	11%	98.8%	11	9.6	
Martitaillite (*) (*): Elution for 22 days	C10	220-270	1.0	31%	30%	98.2%	18	24.6	
<i>With regard to nonoxidized SRGO</i>									
Cracking catalyst	C11	13	627	0.3	9%	8%	98.9%	8	7.6

Numbers preceded by "C": Examples not in accordance with the invention.

TABLE 3

Adsorbent	Ex.	%Al2O3 (weight%)	Specific surface (m2/g)	XRF results			Wickbold results			%S removed/ (100- diesel yield)
				Capacit y(mg S/g)	%S removed (%)	% difference [SI] (%)	Diesel yield (%)	%S removed/ (100- diesel yield)	% difference [SI] (%)	
Merck silica 60	C12	529	2.0	100%	95%	97.6%	42	95%	95%	97.6%
Merck silica 10180	C13	750	1.8	100%	100%	97.5%	40	99%	99%	97.5%
Silica/alumina 1	14	13.1	495	3.0	100%	100%	77	94%	94%	98.7%
Silice/alumina 2	15	3.8	417	2.1	86%	86%	52	100%	100%	100%
Silice/alumina 3	16	13	423	1.9	100%	100%	74	100%	100%	100%
Silice/alumina 4	17	13	540	2.5	100%	100%	72	100%	100%	100%
Cracking catalyst	18	13	627	2.7	100%	100%	84	93%	93%	98.8%
Montmorillonite+ activated bauxite (1/1 weight/weight)	C19	220-270	0.9	100%	99%	94.5%	18	99%	99%	94.5%
Montmorillonite + activated bauxite (1/10 weight/weight)	C20	220-270	0.9	100%	100%	75.4%	4	99%	99%	75.4%

Numbers preceded by "C": Examples not in accordance with the invention.

C19 and C20: Tests carried out with physical mixtures of montmorillonite and of bauxite in order to solve the problems of percolation encountered with the montmorillonite (the bauxite is an inert adsorbent which acts as diluent).